



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 205 291

A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86304136.4

(51) Int. Cl.4: D 06 P 1/00

(22) Date of filing: 30.05.86

D 06 P 5/00, C 09 B 69/10

(30) Priority: 12.06.85 GB 8514905

(71) Applicant: IMPERIAL CHEMICAL INDUSTRIES PLC
Imperial Chemical House Millbank
London SW1P 3JF(GB)

(43) Date of publication of application:
17.12.86 Bulletin 86/51

(72) Inventor: Parton, Brian
11 Cheadon Drive South
Bury Lancashire(GB)

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL

(74) Representative: Stephenson, Kenneth et al,
Imperial Chemical Industries PLC Legal Department:
Patents PO Box 6 Bessemer Road
Welwyn Garden City Herts, AL7 1HD(GB)

(54) Colouration process.

(57) A method for the coloration of textile materials which comprises applying thereto by a printing or continuous dyeing technique a coloured polymer containing repeat units derived from at least one organic dye containing two or more polymerisable olefinically unsaturated groups.

COLORATION PROCESS

This invention relates to a coloration process and especially to a process for the printing or continuous dyeing of
5 textiles using coloured polymers.

Dyes containing vinyl, acryloyl and other polymerisable olefinic groups are already known and methods have been proposed for their homopolymerisation and for their copolymerisation with other polymerisable monomers both in the presence and absence of textile or
10 other substrates.

Thus, United Kingdom Patent Specification No.877402 describes the production of coloured polymers, useful as pigments, by copolymerising azo or anthraquinone dyes containing polymerisable olefinic groups with other unsaturated polymerisable compounds.

15 United Kingdom Patent Specification No.914354 describes a process for the simultaneous dyeing and finishing of textiles by applying a coloured polymer which has been obtained by the emulsion copolymerisation of a dye containing a polymerisable olefinic group and an uncoloured polymerisable compound, the applied copolymer then
20 being cross-linked.

United Kingdom Patent Specification No.1036700 describes organic pigments obtained by the homopolymerisation of 1-methacryloylaminoanthraquinone, 1-p-vinylbenzoylaminoanthraquinone and certain derivatives thereof.

25 Other patents, for example United Kingdom Patents 1046751 and 1218547, have described the application of polymerisable dyes containing olefinic groups to textile materials in conjunction with a free radical polymerisation initiator with the object of polymerising the dye on or within the textile fibres.

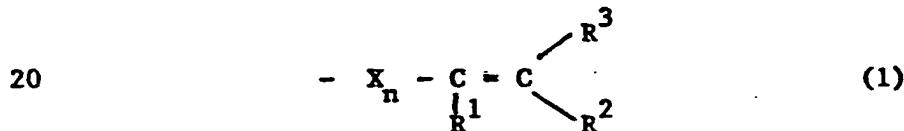
30 Other references to the synthesis, properties and uses of polymeric dyes may be found in a review article by Marechal (Progress in Organic Coatings, 10 (1928) 251-287).

None of the processes described in the above documents appears to have achieved commercial importance, presumably because they did not provide colorations having the intensities and fastness properties that could be obtained more economically by other methods.

5 It has now been found that coloured polymers obtained by polymerising dyes containing two or more polymerisable groups are extremely useful in textile printing and continuous dyeing processes.

Accordingly, the invention provides a method for the coloration of textile materials which comprises applying thereto by a 10 printing or continuous dyeing technique a coloured polymer containing repeat units derived from at least one organic dye containing two or more polymerisable olefinically unsaturated groups.

The polymerisable olefinically unsaturated groups present in the dyes are groups which render the dyes homopolymerisable or 15 copolymerisable with other olefinic (vinyl) monomers under the standard polymerisation conditions. As examples of such groups, there may be mentioned groups of the general formula:

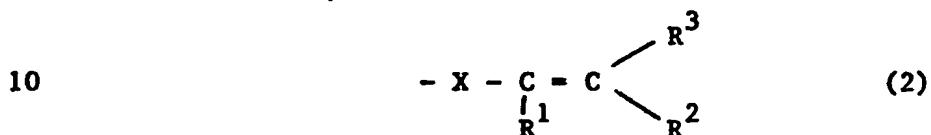


wherein X represents an atom or group linking the olefinic group to a carbon atom present in the dye molecule, n has the value 0 or 1 and 25 each of R¹, R² and R³ independently represents a hydrogen or halogen atom or a hydroxyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkylthio, cycloalkyl, optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylthio, nitro, cyano, acyloxy or 30 alkoxy carbonyl group.

Alkyl groups mentioned herein, either as such or as components of larger groups such as alkoxy carbonyl, particularly include lower alkyl groups having one to four carbon atoms.

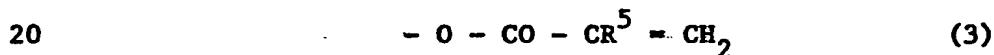
The preferred polymerisable groups are those in which each of R^2 and R^3 is hydrogen and R^1 is hydrogen, halogen, lower alkyl, cyano or alkoxy carbonyl. Especially preferred groups are those in which each of R^2 and R^3 is hydrogen and R^1 is hydrogen, halogen (especially chlorine) or lower alkyl (especially methyl).

As examples of linkages which may be represented by X in the formula:



there may be mentioned $-O-$, $-S-$, $-CO-$, $-CS-$, $-NR^4-CO-$ in which R^4 is hydrogen or alkyl, $-O-CO-$, $-S-CO-$, $-CO-O-$, $-CO-S-$, $-SO-$, $-SO_2-$, $-NR^4-SO_2-$, $-SO_2-NR^4-$, $-CH_2-$, $-O-CH_2-$, $-S-CH_2-$, $-SO_2-CH_2-$, $-COCH_2-$, $-O-CO-CH_2-$, $-NR^4-CH_2-$ and $-NR^4-$.

As examples of especially preferred polymerisable groups there may be mentioned groups of the formula:



in which R⁵ represents hydrogen or lower alkyl, especially methyl.

It is preferred that the dyes contain two polymerisable groups, although dyes containing a higher number of polymerisable groups, for example five, may be used.

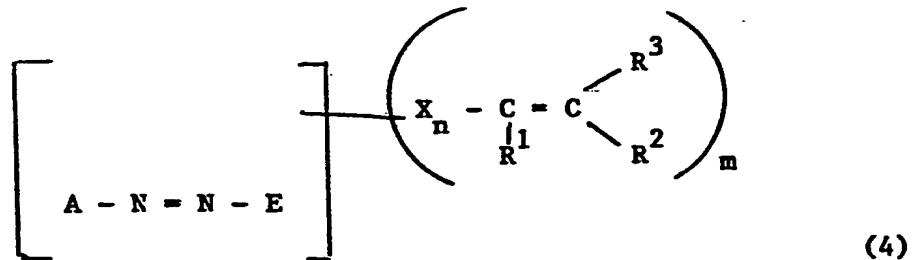
The dye or dyes from which the coloured polymers are derived may belong to any of the classes of organic dyes. As examples of chemical classes, there may be mentioned azo, which may be monoazo or polyazo, anthraquinone, phthalocyanine, triarylmethane, methine, nitro, oxazine including triphenodioxazine, diazahemicyanine, quinophthalone, benzodifuranone and indigoid.

The dyes may be water-soluble due to the presence of solubilising groups such as sulpho, carboxy and quaternary ammonium groups but they are preferably free of such constituents. Other

substituents, conventional to organic dye molecules may be present and these include chlorine and bromine atoms and nitro, cyano, hydroxy, optionally substituted amino, optionally substituted alkyl, alkoxy, optionally substituted aryl, alkylsulphonyl, arylsulphonyl, 5 optionally substituted carbamoyl, optionally substituted sulphamoyl, trifluoromethyl, acylamino, acyloxy, alkylcarbonyl and alkoxy carbonyl groups. Where appropriate, as in phthalocyanine and certain azo structures, the dye molecule may contain a co-ordinately bound metal atom such as copper, chromium or cobalt.

10 Azo dyes from which the coloured polymers may be derived include those of the formula:

15



wherein A represents the residue of a carbocyclic or heterocyclic 20 diazotisable amine containing at least one electron-withdrawing substituent, E represents the residue of a carbocyclic or heterocyclic coupling component, m is an integer of at least 2, and R¹, R², R³, X and n have the meanings given above.

As examples of carbocyclic radicals which may be represented 25 by A, there may be mentioned naphthyl and, especially, phenyl radicals. Heterocyclic radicals which may be represented by A include

- 2-thienyl,
- 3- or 4-pyrazolyl,
- 30 2- or 5-imidazolyl,
- 3-(1,2,4-triazolyl),
- 5-(1,2,3,4-tetrazolyl),
- 2-(1,3,4-thiadiazolyl),
- 3- or 5-(1,2,4-thiadiazolyl),

4- or 5-(1,2,3-thiadiazolyl),
 3-, 4- or 5-isothiazolyl,
 3-pyridyl,
 2-benzoxazolyl,
 5 3-thienyl-[2,3-b]-pyridine,
 3-isothiazolyl-[3,4-d]-pyrimidine,
 3-isothiazolyl-[3,4-b]-pyridine,
 3-isothiazolyl-[3,4-b]-thiophene,
 2-thiazolyl,
 10 2-benzthiazolyl,
 indazol-3-yl,
 pyrazolopyridin-3-yl, and benz-2,1-isothiazol-3-yl radicals.

As examples of electron-withdrawing (electron-attracting) substituents which may be present on A, there may be mentioned
 15 chloro, bromo, fluoro, nitro, cyano, thiocyanato, trifluoromethyl, alkylcarbonyl (e.g. acetyl), alkylsulphonyl (e.g. methylsulphonyl), alkoxy carbonyl (e.g. methoxycarbonyl, ethoxycarbonyl), arylcarbonyl (e.g. benzoyl), arylsulphonyl (e.g. phenylsulphonyl), carbamoyl, alkylcarbamoyl (e.g. methylcarbamoyl), dialkylcarbamoyl (e.g.
 20 diethylcarbamoyl), arylcarbamoyl, diarylcarbamoyl, sulphamoyl, alkylsulphamoyl (e.g. ethylsulphamoyl), dialkylsulphamoyl (e.g. dimethylsulphamoyl), arylsulphamoyl, diarylsulphamoyl and arylazo. For improved light fastness, it is preferred that A does not carry a nitro group when E is carbocyclic and when both A and E are
 25 carbocyclic, it is preferred that A does not contain nitro or chloro unless another different electron-withdrawing group is also present.

In addition to carrying one or more electron-withdrawing substituent, the residue represented by A may carry one or more substituents which are not electron-withdrawing in character.
 30 Examples of such substituents include hydroxy, alkyl (e.g. methyl, butyl), alkoxy (e.g. methoxy) and acylamino (e.g. acetylamino) radicals.

The residue of the coupling component represented by E may be the residue of any of the carbocyclic or heterocyclic coupling

comp nents, that is to say compounds which couple with diaz compounds to form azo dyes. Examples of such coupling components include members of the phenol, naphthol, arylamine, pyrazolone, aminopyrazole, 2,6-diaminopyridine, 2,6-dihydroxypyridine and 5 aminopyrimidine series. Any of the substituents appropriate to coupling components may be present.

Anthraquinone dyes from which the coloured polymers may be derived particularly include derivatives of 1,4-, 1,5- and 1,8-diaminoanthraquinone.

10 The polymers may be prepared by polymerising at least one organic dye containing two or more polymerisable olefinically unsaturated groups. The polymerisation may be carried out using any of the appropriate conventional methods. Thus, bulk, solution, emulsion or suspension techniques may be used with the usual 15 polymerisation initiators and, where necessary, emulsifiers and/or protective colloids. To obtain the polymers in solid particulate form, it is convenient to carry out the polymerisation in an organic solvent using a suitably soluble initiator such as azo-diisobutyronitrile and isolate the copolymer by precipitation and 20 filtration. Polymers can be obtained in a convenient stable dispersion (latex) form using emulsion polymerisation techniques and, for example, a persulphate as initiator.

Especially useful coloured polymers for use in the method of the invention may be prepared by copolymerising at least one organic 25 dye containing two or more polymerisable olefinically unsaturated groups and at least one uncoloured polymerisable olefin. The copolymerisation may be carried out using the conventional methods described above to give copolymers containing repeat units derived from the organic dye and from the uncoloured olefin. The copolymers 30 suitably contain at least 0.5% and preferably from 2 to 10% on a weight basis of unit derived from the organic dye.

Examples of uncoloured polymerisable olefins which may be used in preparing the coloured polymers include vinyl aromatic compounds, for example, styrene, alpha-methylstyrene and vinyl

t luene, alpha-beta-unsaturated carb xylic acids, for example acrylic and methacrylic acids and the nitriles, amides and esters thereof, for example, acrylonitrile, methyl methacrylate, butyl methacrylate, glycidyl methacrylate, acrylamide and N-methylolacrylamide, vinyl esters, for example vinyl acetate, vinyl chloride, vinylidene chloride, vinyl carbazole and vinyl ketones. Methacrylic acid esters such as methyl methacrylate are preferred.

Dyes containing two or more polymerisable olefinically unsaturated groups are known in the art and may be prepared by introducing polymerisable groups into a dye or into one or more of the intermediates therefor, for example the diazotisable amine and/or the coupling component in the case of an azo dye. In one method of introduction, a dye or intermediate containing an appropriate functional group is reacted with a compound containing a polymerisable olefinic group and a functional group which is reactive towards the aforementioned functional group.

The coloured polymers are particularly useful in the form of latices containing from 20 to 50% by weight of the polymer. An especially useful latex contains from 20 to 50% by weight of a copolymer containing from 2 to 10% by weight of units derived from an organic dye having at least two methacryloyl groups and from 98 to 90% by weight of units derived from a mixture of co-monomers consisting of methyl methacrylate and an N-methylolacrylamide derivative which latter comprises from 0.1 to 5.0%, preferably from 0.5 to 2.0%, by weight of the co-monomer mixture. The dye preferably contains two methacryloyloxy groups and the N-methylolacrylamide derivative is especially N-methylolacrylamide itself.

Textile materials which may be coloured by the method of the invention include both natural and artificial textile materials, for example textile materials comprising natural cellulose fibres, for example cotton, flax, jute, hemp, sisal and ramie, regenerated cellulose fibres, for example viscose rayon and cuprammonium rayon, cellulose ester fibres, for example cellulose acetate and cellulose

triacetate, natural or protein fibres, for example wool, silk and mohair, regenerated protein fibres, synthetic polyamide fibres, for example nylon 66 and nylon 6, modified synthetic polyamide fibres, aromatic polyester fibres, for example polyethylene terephthalate, 5 modified polyester fibres, polyacrylonitrile fibres, modified polyacrylonitrile fibres, polyurethane fibres and polyolefin fibres, for example polypropylene and fibres based on other synthetic polymers and copolymers, for example fibres based on copolymers of vinylidene dinitrile and vinyl esters, and blends of the above 10 fibres. The method is of particular value for the coloration of cotton, polyester and polyester/cotton blends.

In a printing process, the coloured polymer, optionally in the form of an aqueous dispersion or latex, may be incorporated into a print paste together with other usual ingredients thereof, the 15 print paste being applied to the textile material in conventional manner. The print pastes may also contain cross-linking agents, binders and catalysts. The resulting prints are superior to those obtained by conventional pigment printing processes in respect of brightness of shade, colour value, fastness to rubbing, fastness to 20 solvents and transparency over pigment black giving sharper lines. The polymers can be used in conjunction with pigments in a conventional pigment printing recipe. Relative to printing processes using disperse or reactive dyes, the method of the invention has the advantage that it is not necessary to wash off or 25 clear after fixation.

In a continuous dyeing process, the coloured polymer is incorporated into a padding liquor together with other usual ingredients thereof, the liquor being applied to the textile material in conventional manner. The padding liquor can contain 30 cross-linking agents, binders and catalysts. The resultant dyeings are bright, have excellent fastness properties and do not require a subsequent clearing process.

The invention is illustrated but not limited by the following Examples in which all parts are by weight.

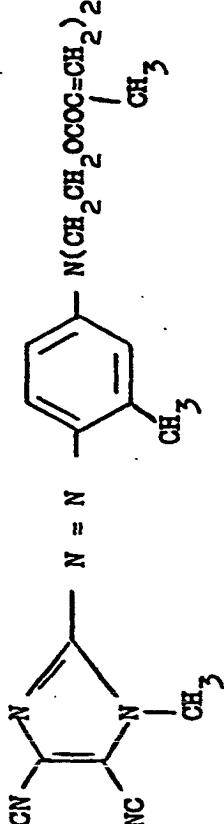
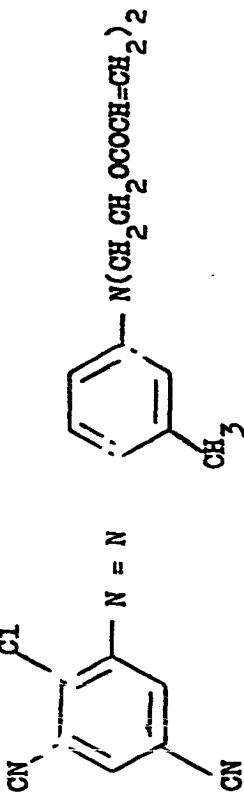
Example 1

1.0 part of 4,6-bis-(beta-acryloyloxyethylamino)-2-ethyl-5-(4-nitrophenylazo)pyrimidine is dissolved in 50 parts of methyl methacrylate then added with rapid stirring to a solution of
5 1.2 parts of the sodium salt of lauryl ether sulphonic acid and 0.4 parts of an ethoxylated C₁₃-C₁₅ aliphatic alcohol in 20 parts of water to give a coarse emulsion. This coarse emulsion is treated with 4.6 parts of 4% aqueous potassium persulphate then added portionwise over 15 minutes to a solution of 3.5 parts of 4% aqueous
10 potassium persulphate and 0.3 parts of the sodium salt of lauryl ether sulphonate in 33 parts of water at 88-90°C. After stirring at 88-90° for a further 10 minutes the mixture is cooled to room temperature, screened then applied to polyester and cotton using conventional printing and continuous dyeing techniques to yield a
15 golden yellow shade of excellent fastness to light, heat and wet treatments. When applied to cotton in the presence of a butyl acrylate based polymeric binder system excellent fastness to wet and dry rubbing is also obtained.

The following table gives further Examples of products obtained in a similar way to the product of Example 1. Column 2 indicates the dyestuff monomer used, Column 3 the colourless co-monomer and Column 4 the colour of the final print.

| Example | Dyestuff Monomer | Shade on Cotton |
|---------|---|---------------------|
| | Colourless Co-Monomer | |
| 2 | <p style="text-align: center;"> $\text{NHCH}_2\text{CH}_2\text{OCO.C}=\text{CH}_2$ CH_3 $\text{NHCH}_2\text{CH}_2\text{OCO.C}=\text{CH}_2$ CH_3 </p> | Golden yellow |
| 3 | <p style="text-align: center;"> $\text{NHCH}_2\text{CH}_2\text{OCO.C}=\text{CH}_2$ CH_3 </p> | Methyl methacrylate |
| 4 | <p style="text-align: center;"> CH_3 CN $\text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N}(\text{CH}_2\text{CH}_2\text{OCOCH}_2)_2$ </p> | Bluish- |

| Example | Dyestuff Monomer | Colourless Co-Monomer | Shade n Cott n |
|---------|---|-----------------------|-------------------|
| 5 | <p>Chemical structure of Example 5: A diazo monomer with a 4-methylphenyl group attached to the nitrogen atom. The structure is $N\text{-}(\text{4-methylphenyl})\text{-}N'\text{-}(\text{CH}_2\text{CH}_2\text{OCOCH=CH}_2)_2$.</p> | Methyl methacrylate | Orang |
| 6 | <p>Chemical structure of Example 6: A diazo monomer with a 4-methylphenyl group attached to the nitrogen atom. The structure is $N\text{-}(\text{4-methylphenyl})\text{-}N'\text{-}(\text{CH}_2\text{CH}_2\text{OCOCH=CH}_2)_2$.</p> | " | Violet |

| Example | Dyestuff Monomer | Colourless Co-Monomer | Shade on Cotton |
|---------|---|-----------------------|-----------------|
| 7 |  <p>Chemical structure of Example 7: A triazine ring substituted with a cyano group (CN) at position 2, a methyl group (CH₃) at position 4, and a 4-(methylamino)-N-(2-methacryloyloxyethyl)-N-(2-methacryloyloxyethyl) group at position 6.</p> | Methyl methacrylate | Bluish-red |
| 8 |  <p>Chemical structure of Example 8: A triazine ring substituted with a chlorine atom (Cl) at position 2, a cyano group (CN) at position 4, and a 4-(methylamino)-N-(2-methacryloyloxyethyl)-N-(2-methacryloyloxyethyl) group at position 6.</p> | " | Orange |

| Example | Dyestuff Monomer | Colourless Co-Monomer | Shade on Cotton |
|---------|------------------|-----------------------|-----------------|
| 9 | | Methyl methacrylate | Reddish-orange |
| 10 | | " | Bluish-red |

| Example | Dyestuff Monomer | Colourless Co-Monomer | Shade on Cotton |
|---------|--|-----------------------|-----------------|
| 11 | <p style="text-align: center;"> $\text{C}_6\text{H}_4\text{N}(\text{Ph})\text{NO}_2 - \text{C}_6\text{H}_3(\text{CN})\text{N}(\text{HCH}_2\text{CH}_2\text{OCOCH=CH}_2) - \text{C}_6\text{H}_3(\text{NHCH}_2\text{CH}_2\text{OCOCH=CH}_2)\text{N}$ </p> | Methyl methacrylate | Orange |

Table 2 describes further Examples of coloured copolymers prepared by the method of Example 1. In the table, the second and third columns respectively describe the diazo and coupling components used to make the azo dye. The third column gives the colourless co-monomer and the final column indicates the colour of the printed cotton.

Table 2

| <u>Example</u> | <u>Diazo Component</u> | <u>Coupling Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|------------------------|--|---|------------------------|
| 10 | | | | |
| 12 | 4-nitroaniline | 4,6-bis-[(2-acryloyloxy-1-ethyl)ethylamino]-2-ethylpyrimidine. | methyl methacrylate (mm) | Golden yellow |
| 15 | " | " | mm/acrylic acid | " |
| 20 | 14 | " | mm/butyl acrylate | " |
| 25 | 15 | " | 2-ethyl hexyl methacrylate | " |
| 30 | 16 | " | dodecyl methacrylate | " |
| 35 | 17 | 4-(1,1-bis-acryloyloxy-methylpropoxy-carbonyl)aniline | 1-ethyl-5-cyano-4-methyl-6-hydroxypyrid-2-one | mm Greenish yellow |
| 35 | 18 | 3,4-dicyanoaniline | 3-methyl-N,N-bis-acryloyloxyethyl-aniline | mm Orange |

| <u>Example</u> | <u>Diaz Component</u> | <u>Coupling Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|---------------------------------|--|---|------------------------|
| 5 19 | 2-cyano-4-nitroaniline | 3-methyl-N,N-bis-acryloyloxyethyl-aniline | mm | Bluish red |
| 10 20 | 2-chloro-4-nitroaniline | " | mm | Red |
| | 21 | 4-chloro-2,6-dicyanoaniline | " | Red |
| 15 22 | 2,6-dicyano-4-methylaniline | " | mm | Red |
| | 23 | 4-chloro-2-nitroaniline | " | mm |
| 20 24 | 2-chloro-6-cyano-4-nitroaniline | 3-acetylamo-N,N-bis-acryloyloxyethylaniline | mm | Blue |
| 25 25 | 2-chloro-4-nitroaniline | N,N-bis-acryloyloxyethylaniline | mm | Orange |
| | 26 | 4-(N,N-bis-2-acryloyloxyethylsulphamoyl)-2-nitroaniline | 2-naphthol | mm " |
| 30 | 27 | 4-(N,N-bis-2-acryloyloxyethylsulphamoyl)-2,6-dichloroaniline | N,N-bis-acryloyloxyethylaniline | mm Golden yellow |
| 35 | 28 | 2,3,5-trichloro-6-cyanoaniline | 3-methyl-N,N-bis-acryloyloxyethyl-aniline | mm Orange |
| 40 | 29 | 5-amino-4-cyano-1,3-dimethyl pyrazole | N-acryloyloxyethyl-N-cyanoethyl-3-acrylamidoaniline | mm Golden yellow |
| 45 | 30 | 3-chloro-4-cyanoaniline | 3-methyl-N,N-bis-acryloyloxyethyl-aniline | mm Orange |

| <u>Example</u> | <u>Diaz Component</u> | <u>Coupling Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|-----------------------|---------------------------|------------------------------|------------------------|
|----------------|-----------------------|---------------------------|------------------------------|------------------------|

5 31 4-aminoazobenzene "

32 3,5-dicyanoaniline "

The following Table 3 represents polymerised dye emulsions obtained in a similar fashion by using the coupling component of Example 35 and the diazo component described in the second column. The colourless co-monomer is again described in column three and the shade imparted to cotton is shown in the final column.

Table 3

| <u>Example</u> | <u>Diazo Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|--|------------------------------|------------------------|
| 15 | 33 2,5-dichloro-4-cyanoaniline | mm | Orange |
| 20 | 34 2,6-dicyano-4-ethoxycarbonyl-3-methylaniline | mm | Bluish red |
| 25 | 35 3-amino-5-cyano-6-methylisothiazolo[3,4:b]pyridine | mm | Blue |
| 30 | 36 2-amino-6-thiocyanatobenzthiazole | mm | Red |
| | 37 2-amino-5-chloro-1,3-thiadiazole | mm | Scarlet |
| 35 | 38 4-ethylsulphamoylaniline | mm | Golden yellow |
| | 39 4-methoxycarbonylaniline | mm | " |
| 35 | 40 4-butoxycarbonylaniline | mm | " |
| | 41 4-methylsulphonylaniline | mm | Orange |
| 40 | 42 2-cyano-4-methoxycarbonylaniline | mm | Red |
| | 43 2-chloro-6-cyano-4-methoxy-carbonylaniline | mm | Red |
| 45 | 44 2,6-dicyano-4-methoxycarbonyl-aniline | mm | Violet |

| <u>Example</u> | <u>Diaz Comp nent</u> | <u>Col urless co-monom r</u> | <u>Shad on c tton</u> |
|----------------|--|----------------------------------|-------------------------------|
| 5 45 | 2-amino-3-cyano-5-phenylazo-thiophene | mm | Blue |
| | 46 2-chloro-5-nitroaniline | mm | Yellow |
| 10 47 | 4-bromo-2,6-dicyanoaniline | mm | Red |
| | 48 2-amino-3-cyano-4-ethoxycarbonyl-aniline | mm | Red |
| 15 49 | 5-amino-3-cyanomethyl-4-ethoxy-carbonyl-1-methylpyrazole | mm | Orange |
| | 50 5-amino-3-phenyl-1,2,4-thiadiazole | mm | Red |
| 20 51 | 5-amino-3-methylthio-1,2,4-thiadiazole | mm | Red |
| | 52 5-amino-4-nitro-3-methyl-isothiazole | mm | Reddish blue |
| 25 53 | 5-amino-3-bromo-4-acetyl-isothiazole | mm | Red |
| | 54 6-amino-2-methylthio-isothiazolo[4,5:d]thiazole | mm | Red |
| 30 | 55 3-amino-4-methyl-5-methylthio-isothiazole | mm | Golden yellow |
| | 35 56 4-amino-3,5-bis-ethoxycarbonyl-isothiazole | mm | Scarlet |
| | 57 2-amino-4-chloro-5-formylthiazole | mm | Violet |
| 40 58 | 5-amino-4-cyano-3-methylsulphonyl-isothiazole | mm | Bluish red |
| | 59 5-amino-4-cyano-3-ethylsulphonyl-isothiazole | mm | " |
| 45 | 60 3-amino-2,4,6-trichloropyridine | mm | Orange |

| <u>Example</u> | <u>Diazo Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|---|------------------------------|------------------------|
| 5 61 | 2-amino-4,5-dicyanothiazole | mm | Reddish blue |
| 62 | 2-amino-6-cyanobenzthiazole | mm | Bluish red |
| 10 63 | 3-amino-5,7-dicyano-2,1-benzisothiazole | mm | Blue |
| 15 64 | 2-cyano-3,5-bistrifluoromethyl-aniline | mm | Red |

Similar dyes are prepared by using the coupling component of Example 1 with the diazo components indicated in Table 4. The shades obtained on cotton are indicated in the final column of the table. All of the co-polymerised dyes are made using the quantities described in Example 1.

Table 4

| <u>Example</u> | <u>Diazo Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|--------------------------------|------------------------------|------------------------|
| 25 65 | 2-chloro-4-nitroaniline | mm | Orange |
| 30 66 | 2-cyano-4-nitroaniline | mm | Reddish orange |
| 35 67 | 2-bromo-6-cyano-4-nitroaniline | mm | Yellow red |
| 40 68 | 2,6-dicyano-4-nitroaniline | mm | Scarlet |
| 69 | 4-ethylsulphamoylaniline | mm | Yellow |
| 70 | 3,4-dicyanoaniline | mm | Golden yellow |

| <u>Example</u> | <u>Diazo Component</u> | <u>C lourless c -m nomer</u> | <u>Shade on cotton</u> |
|----------------|---|---------------------------------------|--------------------------------|
| 5 71 | 4-nitroaniline | mm/N-methyloacrylamide | " |
| | 72 | 2-chloro-5-nitroaniline | mm |
| 10 73 | 4-methoxycarbonylaniline | mm | Mid-yellow |
| | 74 | 2,6-dichloro-4-ethylsulphamoylaniline | mm |
| 15 75 | 2-bromo-6-cyano-4-methoxy-carbonylaniline | mm | Orange |
| 20 76 | 5-amino-4-cyano-3-methylisothiazole | mm | Scarlet |
| | 77 | 4-methylsulphonylaniline | mm |
| 25 78 | 2-amino-3-cyano-5-phenylazo-thiophene | mm | Scarlet |
| | 79 | 2,6-dicyano-4-methylaniline | mm |
| 30 80 | 2,6-dicyano-4-methoxycarbonylaniline | mm | Scarlet |
| | 81 | 2-cyano-5-nitroaniline | mm |
| 35 82 | 2-methoxycarbonyl-4-nitroaniline | mm | " |

Example 83

A preparation is conducted in exactly the same way as in Example 1 except that 3.0 parts of the same dyestuff monomer is used in place of the 1.0 part of Example 1 to give a final print on 5 cotton with good handle properties.

Example 84

A further preparation is conducted as described in Example 86 except that 1 part of N-methyol acrylamide is additionally dissolved in the solution containing the surfactants 10 (lauryl ether sulphonate and ethoxylated C₁₃-C₁₅ aliphatic alcohol). The final emulsion is applied to cotton in the presence of synthetic thickener alone and fixed by baking at 150°. The resultant print has good handle properties and fastness to scrubbing and rubbing.

Further examples are illustrated in the following Table 5.
15 The diazo component is shown in the second column, the coupling component in the third column, the co-monomer in the fourth column and the shade imparted to cotton in the fifth column. The method of preparation is as described for Example 1.

Table 5

| | <u>Example</u> | <u>Diazo Component</u> | <u>Coupling Component</u> | <u>Colourless co-monomer</u> | <u>Shade on cotton</u> |
|----|----------------|-------------------------|---|------------------------------|------------------------|
| 5 | 85 | 2-chloro-4-nitroaniline | 1-[2,3- <u>bis</u> (acryloyl oxy)prop-1-yl]-3-cyano-2-hydroxy-4-methylpyrid-6-one | mm | Greenish yellow |
| 10 | 86 | " | 1-[4-N:N- <u>bis</u> (2-acryloyloxyethyl)sulphamoyl]phenyl-5-hydroxy-4-methylpyrazole | mm | " |
| 15 | 87 | " | 2-(N,N- <u>bis</u> -2-acryloyloxyethyl)-carbamoyl-3-naphthol | mm | Scarlet |
| 20 | 88 | " | 4,6- <u>bis</u> -(2-acryloyloxyethyl-amino)-2-chloropyrimidine | mm | Golden yellow |
| 25 | 89 | " | 2,4,6-tris(2-acryloyloxyethyl-amino)-2-chloropyrimidine | mm | Orange |
| 30 | 90 | " | 4,6-bis(2-acryloyloxyethyl-amino)-2-thiomethylpyrimidine | mm | " |
| 35 | 91 | " | 4,6- <u>bis</u> (2-acryloyloxyethyl-amino)-2-N,N- <u>bis</u> -ethylamino pyrimidine | mm | Scarlet |
| 40 | | | | | |

| <u>Example</u> | <u>Diazo Component</u> | <u>Coupling Component</u> | <u>Colorless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|-------------------------|--|-----------------------------|------------------------|
| 5 92 | 2-chloro-4-nitroaniline | 5-(2,3-bis-acryloyloxy)prop-1-ylamino-1,3-dimethylpyrazole | mm | Golden yellow |
| 10 93 | " | 2,6-bis(2-acryloyloxyethyl-amino)-3-cyano-4-methylpyridine | mm | Orange |
| 15 94 | " | 2-chloro-N-(2,3-bis-acryloyloxy-prop-1-yl)aniline | mm | Golden yellow |
| 20 95 | " | 2-chloro-N-(2,3-bis-acryloyloxy-prop-1-yl)aniline | mm | " |
| 25 96 | 4-nitroaniline | 2,4-bis-(2-acryloyloxyethyl-amino)-4-chloropyrimidine | mm | " |
| 30 97 | " | 2,4,6-tris-(2-acryloyloxyethyl-amino)-pyrimidine | mm | " |
| 35 98 | " | 2,6-bis(2-acryloyloxyethyl-amino)-3-cyano-4-methylpyridine | mm | Orange |
| 40 99 | 4-nitroaniline | 1-[2,3-bis(acryloyl oxy)prop-1-yl]-3-cyano-2-hydroxy-4-methylpyrid-6-one | mm | Greenish yellow |

| <u>Example</u> | <u>Diazo Component</u> | <u>Coupling Component</u> | <u>Colorless c-monomer</u> | <u>Shade on cotton</u> |
|----------------|--|--|------------------------------------|--------------------------------|
| 5 100 | 4-(N,N-bis-2-acryloyloxyethyl)sulphamoyl-2-chloroaniline | N,N,N'-tris(2-acryloyloxyethyl)-1,3-phenylene diamine | mm | Scarlet |
| 10 101 | " | 5-acryloylamino-2-methoxyl-N,N-bis-2-acryloyloxyethylaniline | mm | Red |
| 15 102 | " | N-(2-acryloyloxyethyl)-N-(2-cyanoethyl)-3-methylaniline | mm/bis-acryloyl ethylene glycol | Orange |
| 20 103 | 4-aminostyrene | 1-(3-acryloyloxy-n-propyl)-3-cyano-2-hydroxy-4-methylpyrid-6-one | " | Greenish yellow |
| 25 104 | 4-acryloyloxyethylamino sulphonylaniline | " | " | " |
| 30 105 | 2-chloro-4-nitroaniline | N,N-bis-(2-acryloyloxyethyl)aniline | butyl methacrylate | Orange |
| 35 106 | " | 4,6-bis-(2-methacryloyloxyethylamino)-2-ethylpyrimidine | 2-ethyl hexyl methacrylate/mm. 2/1 | " |
| 40 107 | " | " | Styrene/mm. 1/3 | " |
| 40 108 | " | " | alpha-methyl styrene | " |
| 45 109 | " | " | methacrylonitrile | " |

| <u>Example</u> | <u>Diazo Component</u> | <u>Coupling Component</u> | <u>Colorless co-monomer</u> | <u>Shade on cotton</u> |
|----------------|-------------------------|---|---------------------------------|------------------------|
| 5 110 | 2-chloro-4-nitroaniline | 4,6-bis-(2-methacryloyloxyethylamino)-2-ethylpyrimidine | mm/glycidyl methacrylate 4/1 | " |
| 10 111 | " | " | vinyl acetate/mm. 1/2 | " |
| 15 112 | " | " | dodecyl methacrylate | " |
| 20 113 | 4-nitroaniline | 4,6-bis-(2-acryloyloxyethylamino)-2-ethylpyrimidine | mm | " |
| 25 114 | " | 4,6-bis-(2-methacryloyloxyethylamino)-2-ethylpyrimidine | mm | " |
| 30 115 | 2-cyano-4-nitroaniline | N,N-bis-[2-(2-carboxyacryloyloxy)ethyl]-3-methylaniline | mm | Bluish red |
| 35 116 | 4-nitroaniline | 4,6-bis-[2-(1-bromoacryloyloxyethylamino)-2-ethylpyrimidine | mm | Golden yellow |
| 40 117 | " | 4,6-bis-[2-(1-methoxyacryloyloxyethylamino)-2-ethylpyrimidine | mm | " |

The Examples given below in Table 6 are emulsion c -polymers of methyl methacrylate.

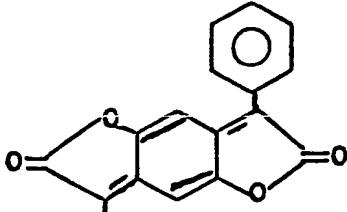
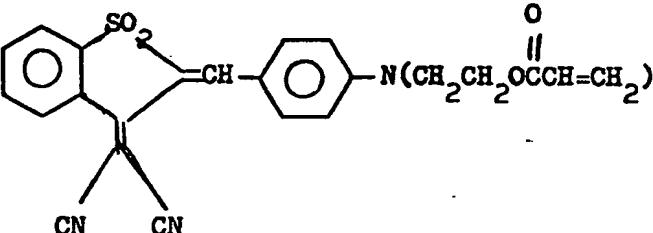
Table 6

5

| | <u>Example</u> | <u>Dyestuff Monomer</u> | <u>Shade on cotton</u> |
|----|----------------|--|------------------------|
| 10 | 118 | 1,4- <u>bis</u> -(2-acryloyloxyethylamino)-anthraquinone | Reddish blue |
| | 119 | 1,4- <u>bis</u> -(2-acryloyloxy-1-ethylethylamino)-anthraquinone | " |
| 15 | 120 | 1,4- <u>bis</u> -[4-(2-acryloyloxyethoxy)phenyl-amino]anthraquinone | Green |
| 20 | 121 | 1,4- <u>bis</u> -(2-acryloyloxyethylamino)-5-hydroxy-8-nitroanthraquinone | Turquoise |
| | 122 | 1,5- <u>bis</u> -(2-acryloyloxyethylamino)-anthraquinone | Red |
| 25 | 123 | 2-(4-acryloyloxyphenoxy)-4-acryloylamino-1-aminoanthraquinone | Red |
| | 124 | 1,4- <u>bis</u> -(4-acryloyloxymethyl-2,6-dimethylanilino)anthraquinone | Reddish blue |
| 30 | 125 | 1-[2-(1,1-acryloyloxymethyl)propoxy-carbonylethylamino]-4-amino-8-hydroxy-5-nitroanthraquinone | Turquoise |
| 35 | 126 | 1,8- <u>bis</u> -(2-acryloyloxyethylamino)-4,6-dihydroxyanthraquinone | Greenish blue |
| | 127 | 1,4- <u>bis</u> -(2-acryloyloxyethylamino)-5,8-dihydroxyanthraquinone | " |

| | <u>Example</u> | <u>Dy stuff Monomer</u> | <u>Shade n cotton</u> |
|----|----------------|---|---------------------------|
| 5 | 128 | 1,5-bis-(2-acryloyloxyethylamino)-4,8-dihydroxyanthraquinone | " |
| | 129 | 1,8-bis-(2-acryloyloxyethylamino)-anthraquinone | Red |
| 10 | 130 | 4-acryloylamino-2-(2-acryloyloxyethoxy)-1-aminoanthraquinone | Red |
| 15 | 131 | 1,5-bis-(2-acryloyloxyethylamino)-naphtha-4,8-diquinone | Blue |
| | 132 | 1,5-bis-(2-acryloyloxyethylamino)-dibromonaphtha-4,8-diquinone | Greenish blue |
| 20 | 133 | 2-[4-N:N-bis-(2-acryloyloxyethylamino)-phenylazo]-6-methoxy-3-methylbenzthiazolouine methosulphate | Blue |
| 25 | 134 | 3-[4-N:N-bis-(2-acryloyloxyethylamino)-phenylazo]-2,4-dimethylthiazolium methosulphate | Red |
| 30 | 135 | $\text{CH}_3 \text{N}^+ \text{---} \text{C}(\text{CH}_3)_2 \text{---} \text{CH}=\text{N}-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_5-\text{OCH}-\text{CH}(\text{OOCCH}=\text{CH}_2)-\text{CH}_2\text{OCOCH}=\text{CH}_2$ | Yellow |
| 35 | | CH_3SO_4^- | |
| 40 | 136 | Copper phthalocyanine- $(\text{SO}_3\text{H})_2(\text{SO}_2\text{NCH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2)_2$ | Turquoise |
| | 137 | Copper phthalocyanine- $(\text{CH}_2\text{OCOCH}=\text{CH}_2)_3$ | " |
| 45 | 138 | 4-(2,2-bis-acryloyloxy)methylethoxy)-N-(2,4-dinitrophenyl)aniline | Yellow |

| <u>Example</u> | <u>Dyestuff Monomer</u> | <u>Shad on cotton</u> |
|----------------|--|-----------------------|
| 5 139 | | Greenish yellow |
| 10 | | |
| 15 140 | | Mid-yellow |
| 20 | | |
| 25 | | |
| 30 | | |
| 35 | | |
| 40 | | |
| 141 | 1-[4-N:N-bis-(2-acryloyloxyethyl)amino-phenyl]-2,2-dicyanoethylene | Greenish yellow |
| 142 | 3-[N:N-bis-(2-acryloyloxyethyl)carbamoyl]-1-(2-chloro-s-trifluoromethyl)phenylazo-2-hydroxynaphthalene | Orange |
| 143 | N:N-bis-(2-acryloyloxyethyl)-3-acetylamoно-4-(2-chloro-4-methylsulphonyl)phenylazo-aniline | " |
| 144 | 2-[4-N:N-bis-(2-acryloyloxyethyl)amino]-2-methylphenylazo-6-nitrobenzthiazole | Rubine |
| 145 | | Red |

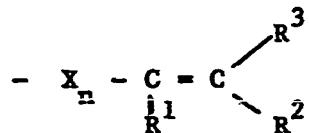
| <u>Example</u> | <u>Dyestuff Monomer</u> | <u>Shade on cotton</u> |
|----------------|---|------------------------|
| 5 146 | 3-[N:N-bis-(2-acryloyloxyethyl)carbamyl]-1-(2-nitro)phenylazo-2-hydroxynaphthalene | Scarlet |
| 10 147 | 5-[4-N:N-bis-(2-acryloyloxyethyl)amino-phenylazo]-3-2-[(1,1-bis-acryloyloxymethyl)propoxycarbonyl]-ethylthio-1,2,4-thiadiazole | Pink |
| 15 148 | N,N-bis-(2-acryloyloxyethyl)-4-(2,6-dichloro-4-nitro)phenylazoaniline | Brown |
| 20 149 |  | Scarlet |
| 25 150 |  | Violet |
| 30 151 | 2,9-bis-(2-acryloyloxyethylamino)-6,13-dichlorotriphenioxazine | Blue |
| 35 | | |
| 40 | | |
| 45 151 | 2,9-bis-(2-acryloyloxyethylamino)-6,13-dichlorotriphenioxazine | Blue |

CLAIMS

1. A method for the coloration of textile materials which comprises applying thereto by a printing or continuous dyeing technique a coloured polymer containing repeat units derived from at least one organic dye containing two or more polymerisable olefinically unsaturated groups.

2. A method according to claim 1 wherein the polymerisable olefinically unsaturated groups in the organic dye have the formula:

10



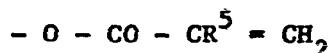
15 wherein X represents an atom or group linking the olefinic group to a carbon atom present in the dye molecule, n has the value 0 or 1 and each of R¹, R² and R³ independently represents a hydrogen or halogen atom or a hydroxyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkylthio, cycloalkyl, 20 optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylthio, nitro, cyano, acyloxy or alkoxycarbonyl group.

25 3. A method according to claim 2 wherein each of R² and R³ is hydrogen and R¹ is hydrogen, halogen, lower alkyl, cyano or alkoxycarbonyl.

4. A method according to claim 3 wherein R¹ is methyl.

5. A method according to claim 2 wherein the polymerisable groups have the formula:

30



wherein R⁵ is hydrogen or lower alkyl.

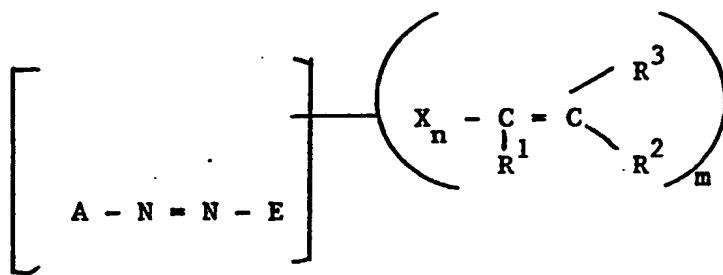
6. A method according to claim 5 wherein R⁵ is methyl.

7. A method according to claim 1 wherein the dye contains two polymerisable olefinically unsaturated groups.

8. A method according to claim 2 wherein the organic dye is an azo dye having the formula:

5

10



wherein A represents the residue of a carbocyclic or heterocyclic diazotisable amine containing at least one electron-withdrawing substituent, E represents the residue of a carbocyclic or

15 heterocyclic coupling component, m is an integer of at least 2, and R¹, R², R³, X and n have the meanings given in claim 2.

9. A method according to claim 1 wherein the coloured polymer contains repeat units derived from at least one organic dye containing two or more polymerisable olefinically unsaturated groups and from at least one uncoloured polymerisable olefin.

20 10. A method according to claim 9 wherein the coloured copolymer contains from 2 to 10% by weight of units derived from an organic dye.

11. A method according to claim 9 wherein the uncoloured 25 polymerisable olefin is methyl methacrylate.

12. A method according to claim 1 wherein the textile material is cotton, polyester or a polyester/cotton blend.

30

KS/BH

27.5.86.